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13. ABSTRACT *(Maximum 200 words)*

The objective of this program includes establishment of a generic method for the growth of single crystal films of important organic materials and measurement of their nonlinear optical properties. In the last three years we have developed a method which is a modification of the "shear method" to prepare single crystal films of specific organic materials having very large second order nonlinearities. This is the first time that single crystal thin films of these organic materials have been prepared. The materials investigated include: i) (N-(4-Nitrophenyl)-L-prolinol) (NPP), ii) (2-cyclooctylamino-5-nitropyridine), (COANP), iii) (8-(4'-acetylphenyl)-1,4-dioxa-8-azspiro[4,5]decane), (APDA) and iv) (4'-N,N-dimethylamino-4-N-methylstilbazolium toluene-p-sulfonate), (DAST). The single crystal films obtained for these materials have excellent optical quality and large areas ($5mm^2$ -$2cm^2$ depending on material). The films were characterized by x-ray diffraction, polarized FTIR, optical absorption and optical microscopy. The second order susceptibilities were measured and very large d-coefficients were observed. Electro-optic measurements have shown extremely large E-O coefficients. The off-resonant nonlinear refractive index of polydiacetylene was measured and picosecond all-optical switching at a high pulse repetition rate (82 MHz) was demonstrated for the first time.

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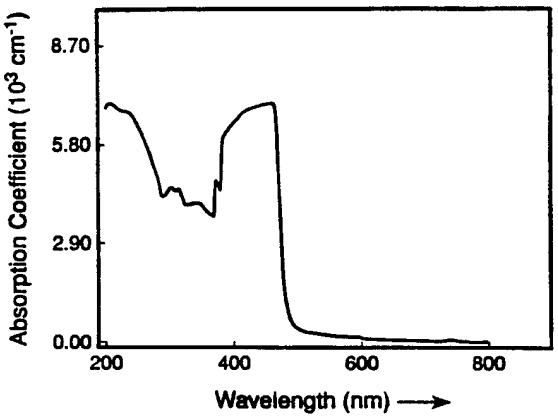
SINGLE CRYSTAL FILMS AND WAVEGUIDES OF ORGANIC MATERIALS; PREPARATION AND NONLINEAR OPTICAL PROPERTIES

(F49620-93-1-0216)

M. Thakur, Auburn University

Final Report

The objective of this program includes establishment of a generic method for the growth of thin single crystal films of important organic nonlinear optical materials and measurement of their nonlinear optical properties. In the last three years we have developed a method which is a modification of the "shear method" to prepare single crystal films of specific organic materials having very large second order nonlinearity. This is the first time that single crystal thin films of organic materials have been prepared. The materials investigated include: i) (N-(4-Nitrophenyl)-L-prolinol) abbreviated as NPP, ii) (2-cyclooctylamino-5-nitropyridine), abbreviated as COANP, iii) (8-(4'-acetylphenyl)-1,4-dioxa-8-azspiro[4,5]decane), abbreviated as APDA, and iv) (4'-N,N-dimethylamino-4-N-methylstilbazolium toluene-p-sulfonate), abbreviated as DAST. NPP has the largest known phase-matchable d-coefficient (about 18 times that of $LiNbO_3$). COANP also has very large d-coefficient. APDA is a new material that is transparent at blue wavelengths and therefore is promising for applications in blue light generation. DAST has very large electro-optic coefficient (about ten times that of $LiNbO_3$). The areas of NPP and COANP films that we have obtained are about $2cm^2$. The APDA film is about 10 mm^2 in area and the DAST films are about $5mm^2$ in area. The crystallographic orientations of these films were determined by x-ray diffraction. The orientations were [101], [100], [100] and [101] for NPP, COANP, APDA and DAST respectively. The films were inspected using optical microscopy under cross-polarization and excellent optical quality was observed.



We have studied the NPP, COANP and DAST films in more detail. The studies included

polarized optical absorption (results shown above for a NPP film), polarized FTIR, x-ray diffraction, nonlinear optical and electro-optic measurements. The spectroscopic and x-ray diffraction measurements have clearly shown that the molecules are oriented perpendicular to the surface of the substrate if the polar group is at the end of the molecule as in COANP. On the other hand if a polar group is oriented sidewise with respect to the molecule as in NPP, then the molecules are oriented parallel to the surface of the substrate. In the case of DAST, a molecular salt, the molecules are oriented at an angle to the substrate surface. Thus as these results show, the molecular orientation is clearly determined by the polar interaction between the molecules and the substrate in the shear-growth scheme. Polarized FTIR spectroscopy of NPP has clearly shown the anisotropy in specific vibration bands of the molecules, consistent with the crystallographic orientation of the films. The SHG studies on COANP and NPP films for various combinations of polarization and electro-optic studies on DAST and NPP were completed. The details of these measurements are discussed in the following.

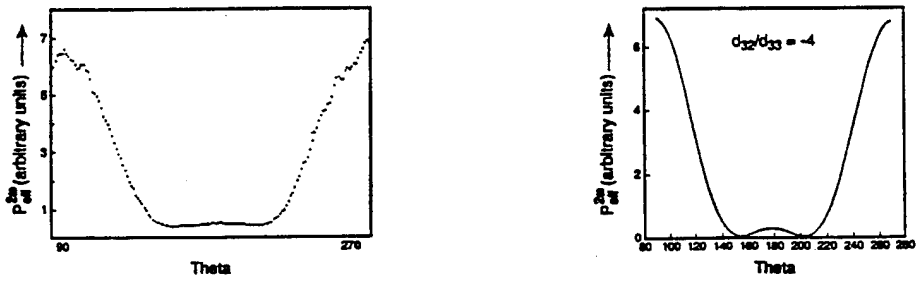


Fig.2 a) The measured SH power of COANP b) The calculated SH power of COANP

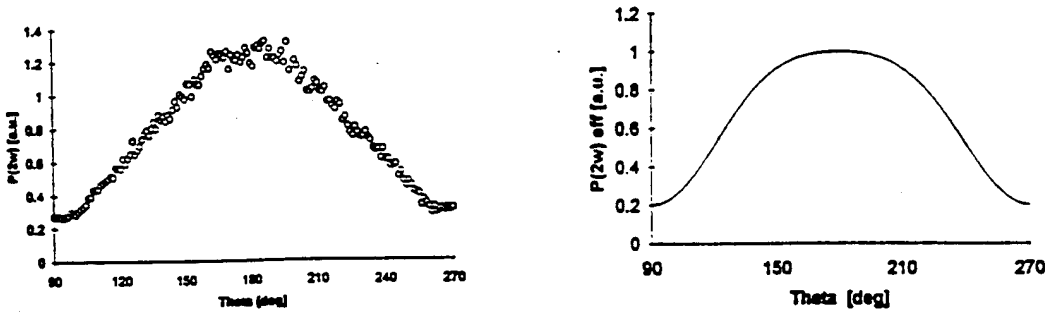
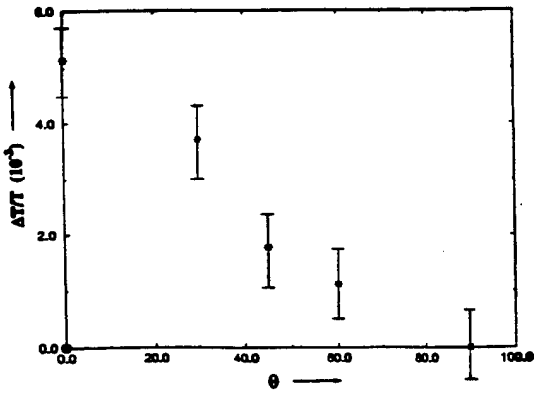


Fig.3 a) The measured SH power of NPP b) The calculated SH power of NPP

The second order optical susceptibilities of NPP and COANP films were measured by second harmonic generation (SHG) using a Nd:YAG laser (30ps, 10Hz). Since the thickness of

these films was less than the typical coherence length ($\sim 20\mu m$), phase-matching was not necessary to consider in analyzing the SHG data. The second harmonic generation measurements were made under various polarization conditions while the film was rotated in a plane perpendicular to the beam. Both the signs and magnitudes of the second order optical tensor elements of the films were measured. The calculated and observed SHG data for COANP and NPP, for a specific polarization condition, are shown in Figs.2&3. The magnitudes of the d-coefficients are: $d_{21}=97pm/V$ and $d_{22}=30pm/V$ for NPP; $d_{32}=56pm/V$ and $d_{32}/d_{33}=-4$ for COANP. The maximum effective d-coefficients for NPP and COANP are 97pm/V and 56pm/V respectively. Thus NPP has a phase-matchable d-coefficient that is 18 times larger than that of $LiNbO_3$.

We have measured the electro-optic effects in NPP and DAST films at $1.06\mu m$ wavelength. As polarized optical microscopy and optical absorption measurements have shown the films are highly birefringent. The electro-optic measurements were made by field induced birefringence studies using ac fields. The molecular orientations on the films were identified by polarized optical microscopy, optical absorption and SHG measurements. Electrodes were applied such that the electric field could be applied at different angles with respect to the molecular axis. The change in transmission ($\Delta T/T$) as a function of the angle (θ) of field orientation relative to the molecular axis was measured for several films and the results for NPP are shown in Fig.1. As expected, the induced birefringence (proportional to $\Delta T/T$), decreased as the angle was increased. The maximum value of the induced birefringence was observed at $\theta = 0$, corresponding to the field oriented parallel to the molecule.



These measurements have shown that the largest E-O tensor element for NPP films, r_{12} is about 65 pm/V. The magnitude of the largest E-O tensor element for the DAST films, r_{11} is about 350 pm/V. These magnitudes are sufficiently large for E-O switching in short waveguides (few mm.) and in the Fabry-Perot geometry. We are presently investing a significant effort in fabrication of waveguides and F-P interferometric structures to demonstrate E-O switching and modulation.

Previously we discussed preliminary results on the fabrication of waveguides on COANP films. We have made further progress in that direction. We are continuing to apply the modified photo-lithographic technique and reactive ion etching to fabricate waveguides. As discussed previously, we use a protective polymer layer to fabricate waveguides on the single crystal films. This protective layer is to guard against any undesired dissolution of the crystal film in solvents used in the photolithographic process. The technique has been successful in preparing channel waveguides. Our preliminary attempt to transmit light through these guides at 1.06μm has been successful. More detailed studies of these guides are in progress. We have recently observed that laser ablation can also be used to fabricate channel waveguides from these films. Using an excimer laser we have successfully etched waveguide structures with reasonably smooth edges. Since this procedure does not require any solvent treatment, no protective layer is necessary. These works are in progress with the objective of demonstrating E-O switching using channel waveguides. Since the required length for a π phase change would be small, the overall loss will also be sufficiently small for applications.

Part of our effort is being invested in studying electro-optic effect in the Fabry-Perot geometry. Therefore we are attempting to grow the films directly on the mirrors that will be used to form the cavity. The F-P structure can be highly efficient in terms of device density and the compact size of devices.

In the third order optics area, we off-resonant nonlinear optical measurements on polydiacetylenes. We have demonstrated all-optical switching using the off-resonant nonlinear refractive index of a PTS crystal (200μm thick) with flat surfaces, placed in a Fabry-Perot cavity. The measurement was made by a pump-probe technique using 90ps pulses. We have observed a 50% modulation depth using a low peak intensity at 1.06μm wavelength. This was the first demonstration of all-optical switching at a high pulse repetition rate (82MHz). Switching at such a high pulse repetition was not possible for semiconductors and multiple quantum wells because those materials have much weaker off-resonant n_2, and therefore measurements were made in the resonant domain leading to substantial thermal effects at a high pulse repetition rate. Recently we have demonstrated all-optical switching for PTS thin films using 30ps pulses from a laser operating at 10Hz. Results of the Fabry-Perot measurements with 90ps pulses are shown in the following. We have also made z-scan measurements on to obtain the sign and magnitude of n_2 and also the magnitude of the two photon absorption coefficient (α_2) at 1.06μm wavelength. The sign was found to be negative consistent with the results of the Fabry-Perot measurements. The negative sign is indicative of the dominance of the bleaching of the exciton over two photon absorption for pumping below the exciton resonance.

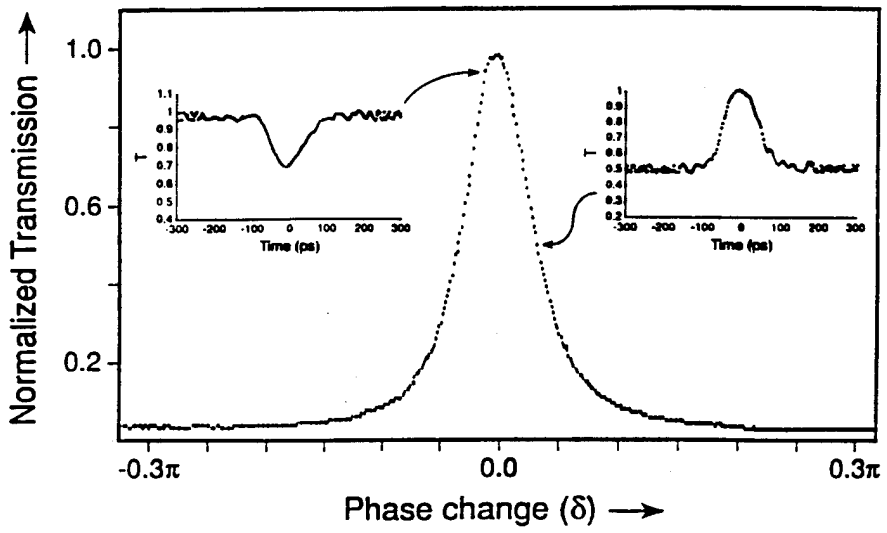


Fig.4 One of the Fabry-Perot fringes measured at a low input intensity. The insets show the changes in transmission as a function of time delay between the pump and probe pulses. The bias points used in the measurement are indicated by arrows. The measured response time was faster than the pulse width used (90ps).

As shown in Fig.4, the measured response time is shorter than the pulse width used (90ps) Similar measurements with 30ps pulses at 10Hz also have shown a pulse-width-limited response time. Clearly, these materials have the best known third order optical characteristics in terms possible applications in ultrafast (picosecond) all-optical switching and modulation at very high repetition rates.

As these results show, we have made significant progress in both the second and third order optics areas, in terms of materials preparation and optical measurements. Our future work will be focussed on further investigation of the method of crystal growth, fabrication of waveguides and other device microstructures and detailed optical measurements. In particular, we will attempt to enhance the areas and the qualities of the single crystal films through more detailed investigations of the growth. For third order optical polymers, polydiacetylenes, we will focus our effort on growing thicker films (thickness $> 25\mu m$) for use in the Fabry-Perot geometry. We will assess different methods of waveguide fabrication, discussed in an earlier section and establish the most appropriate methods to achieve low-loss guiding in the films. We will measure the second and third order optical properties in the films and waveguides at important wavelengths. Various device demonstrations involving nonlinear and electro-optic organic films will result from these studies.

Students Graduated:

This project has partly supported the thesis works of one Ph.D. student (Rafael Quintero-Torres) and one M.S. student (Ananda Mahadevan). Two other Ph.D students (Jianjun Xu and Ligui Zhou) were supported in this program.

Publications:

1) "Picosecond all-optical switching in a Fabry-Perot cavity containing Polydiacetylene", R. Quintero-Torres and M. Thakur, Appl. Phys. Lett., 66 1310 (1995).

2) "Second harmonic generation in single crystal films of an organic material", R. Quintero-Torres and M. Thakur, Opt. Lett., 19 87 (1994).

3) "Preparation of single crystal films of a new organic nonlinear optical material, APDA", Dan Zhi, A. Mahadevan and M. Thakur, Technical Digest, QELS conference, Baltimore, May 24, (1995).

4) "Second order optical studies in single crystal films of NPP", R. Quintero-Torres and M. Thakur, Opt. Lett., accepted.

5) "The sign and magnitudes of the off-resonant nonlinearities of polydiacetylene measured by Z-scan", R. Quintero-Torres and M. Thakur, Mol. Cryst. Liq. Cryst., 256 625 (1994).

6) "Electro-optic effects in single crystal films of NPP", Jianjun Xu, Ligui Zhou and M. Thakur, Appl. Phys. Lett., accepted.

7) "Molecular orientation in single crystal films of NPP", Ligui Zhou and M. Thakur, Chem. Phys. Lett., submitted.

Interactions/Transitions:

1. A collaboration has been initiated with Dr. Kenneth Hopkins at the Wrights Laboratory. The initial objective is to investigate possible use of organic single crystal films in voltage sensing for microelectronic circuits. Since specific organic single crystals have significantly larger E-O coefficients than available commercial materials, there is a clear advantage in using these material films for the stated application.

2. Another collaboration has been initiated with Dr. Kevin Stewart of Molecular OptoElectronics Corp. Dr. Stewart's interest is in using the large area single crystal films of organic E-O materials in tunable filter applications for possible usage in satellite detection systems. Dr. Stewart visited us at Auburn on August 31, 1995, and we discussed this matter in detail. At the request of Dr. Stewart we provided him a large-area ($\sim 1.5 cm^2$) thin film sample of COANP on silicon, for demonstration purposes. Further effort in joint research will be made in the future.